Sorption of Hexane and Cyclohexane Liquids in High Silica Zeolite and Boron-zeotype Materials

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Summary: Pentasil high silica zeolites (ZSM-5, ZSM-11) and their structural analog boron-zeotypes (ZSM5-B, ZSM11-B) and Al-free silicalites have been examined for the sorption of liquid n-hexane and cyclohexane by thermogravimetric constant coverage method. Effect of adsorbates on the framework topology and unit cell dimensions were also studied. The cell volume of boron-substituted samples were found to be significantly smaller than Al-substituted. Crystallinity of the samples were estimated from framework IR spectroscopy, differential thermal analysis, X-ray diffraction and adsorption of n-hexane techniques.

Introduction

Mobil Oil Corporation have recently developed a novel class of high siliceous zeolites, belonging to porotektosilicate family [1]. ZSM-5 and ZSM-11 as well as their pure silica analogues silicalite-1 [2] and silicalite-2 [3] respectively, are members of a distinct family of porotektosilicates named "Pentasils" [4] the structure of which have been published [5]. The framework of which is based essentially on five-membered rings of tetrahedra. The framework structure of porotektosilicate family encloses a two dimensional system of intersecting channels, with 10-membered rings controlling the size of the pore. Both sets of channels in ZSM-11 are straight, whereas in ZSM-5 one set is straight and other one is sinusoidal. The structures of the unit cell of ZSM-5 (silicalite-I) and ZSM-11 (silicalite-2) are schematically shown in Figures 1-5. Although isomorphous substitutions in compact or layered aluminosilicates are quite common, few partial or total substitutions of Si/or Al atoms for boron in open zeolitic framework have been reported elsewhere [6]. In contrast, a number of synthesis of borosilicate molecular sieves with a structure similar to the one of the related Si-rich zeolites ZSM-5, ZSM-11, Silicalite, Beta and Nu-1 have also been reported in the literature [7]. Pentasil-zeolites are gaining tremendous commercial importance as catalysts [8] in a number of hydrocarbon conversion processess, in the production of lower olefine, aromatic and gasoline from methanol and ethanol. When considering catalysis, two main factors play an important role, i.e., the nature of the active sites (acidic sites) and the topology (cavities, channels and pores). When these zeolites are used in the form of granules, there exist both micropores (intracrystalline voids) and macropores (intracrystalline voids) in the zeolite catalyst. Recent studies have shown that the intercrystalline mass transfer plays a very important role in deciding the product distribution of these zeolites [9]. Hence, it is of great interest to know the characteristic of the intercrystalline pores. Many investigations have already been devoted to the modification of zeolites, either during or after their synthesis. The aim was to change their catalytic properties, either by creating active sites or by monitoring the pore size (shape selectivity). For instance, it has been shown that substituting B, Fe, Ga for Al in the pentasil-type zeolites results in a decrease of the acidic strength [10] particularly in the case of boron [11]. Although from the presently available data no major difference in properties appear between the Pentasil-members, the structural differences due to probable framework substitution of Si with B during synthesis suggest that sorption behaviour and shape selectivity properties may be different.
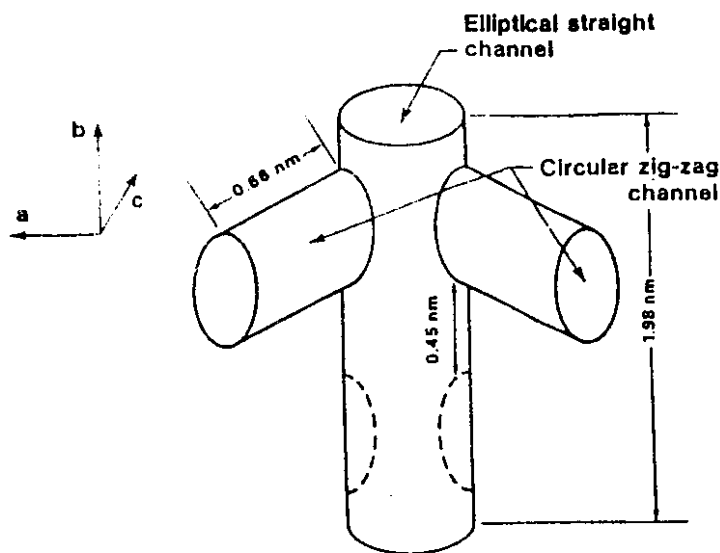
Idealized quarter of a unit cell of silicalite

Fig. 1: Crystal structure of Silicalite-I Silicalite has two pore system, one group of pore is the small, zigzag channels along a-direction   with about circular cross-section of 5.4 ± 0.02Å. The other group is the large, elliptical channels along b-direction with a cross-section of about 5.75 ± 5.15 Å.
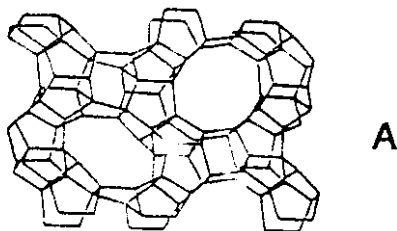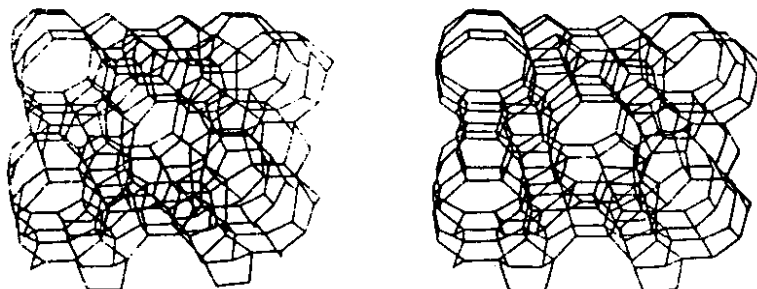

(A): Skeletal diagram of the (010) of ZSM-5 unit cell.
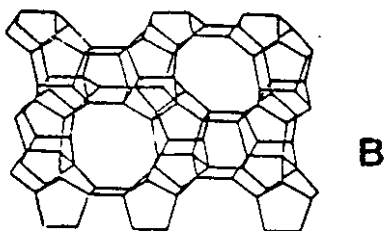
(B): Skeletal diagram of the (100) face of the ZSM-5 unit cell.

Fig. 2:   Crystal structure of ZSM-5

Skeletal diagram of the A and B faces of the
ZSM-11 unit cell. The c-axis is vertical.
Oxygen atoms are not shown.

Fig. 3:   Crystal structure of ZSM-11

(a)   **(b)**
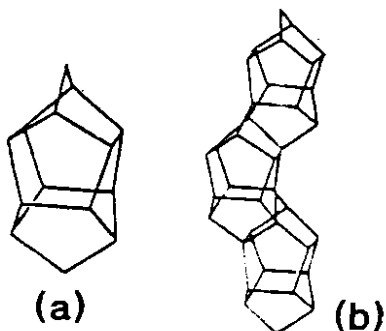
Structural repeating units in the ZSM-5 framework
(a): Secondary building unit
(b): Chain type building block.

Fig. 4:   Building the chain units (b) Found the ZSM 5 and ZSM-11 Structures from the smaller 5-1
secondary building units (a)

Elliptical straight
channels (5.1 x 5.6 Å)

Near circular channels
(5.4 x 5.6 Å)

ZSM5—Al

ZSM11—Al

Fig. 5:   Structure of Pentasil (after KaKatailo and Meier) ZSM-5 and ZSM- 11.

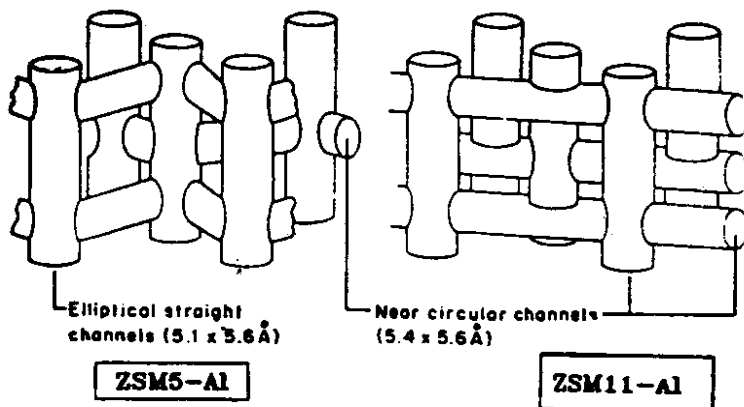Therefore, a study was undertaken to look up the possible differences between ZSM5-Al, ZSM11-Al and their boron-zeotype materials. In this paper the differences in sorptive properties of Pentasil-members for the selected molecules (hexane and cyclohexane) is reported.

Results and Discussion

The four parameters namely (1) XRD intensity of line $2\theta = 22.5°$ (2) the intensity of the framework IR band at 550-575 cm^{-1}, (3) the exothermic peak at 713-723 K and (4) adsorption of n-hexane can all be used for monitoring and characterising the progress of crystallinity of zeolite, zeotype and silicalites [2,4,5]. In Figure 6-7, the X-ray diffraction patterns of (a) ZSM-11 (silicalite-2) and (b) ZSM-5 (silicalite-1) obtained on a PW 1710 Philips X-ray diffractometer (XRD) is shown. Figure 8 portrays the criterion used to differentiate the two varieties which was to make a slow scan past the 45° 2θ region, a single peak identified ZSM-11 (silicalite-2) and a double peak identified ZSM-5 (silicalite-1) [4,5]. The double peaks were always of same relative peak height, indicating no mixture of ZSM-5, ZSM-11 and intermediates. Figures 9-10 illustrate the IR spectra of high silica zeolites, ZSM-5 and ZSM-11. Infrared spectroscopy is useful for quick

identification of materials of the pentasil family [15]. The absorption bands near 550 cm^{-1} has been assigned to the presence of 5-member rings in the structure [15-17]. The structure-sensitivie vibrations near 1200-1225 cm^{-1} and 550 cm^{-1} provide infromation on the diferentiation of these zeolite types in addition to identifying some framework features of zeolites of undetermined crystal structures. The external asymmetric stretching vibration around 1225 cm^{-1} is present in the spectra of structures containing four chain of 5-member rings arranged around a twofold screw axis (ZSM-5 and ZSM-11), as well as the structure with one chain of 5-member rings on the twofold screw axis, as found in the mordenite family [17].

Table 1: Sorporation of n-hexane and cyclo-hexane in aluminosilicate zeolites, boron-zeotype and silicalites

Materails	Mole ratios	Hexane		Cyclohexane	
	Si/M	% Wt. loss	Mol/ Unit cell	% Wt. loss	Mol/unit cell
ZSM5	27.85	11.02	7.64	3.97	2.92
ZSM5-B	20.81	10.89	7.44	3.89	2.65
ZSM11	49.47	11.50	7.94	4.07	2.81
ZSM11-B	37.39	11.01	7.57	3.96	2.72
Silicalite-1	987.00	10.73	8.01	3.92	3.01
Silicalite-2	992.00	10.85	7.93	3.97	2.75

M = Al or B

X-ray diffraction data

Sample		Reference	
d(Å)	I/I°	d(Å)	I/I°
10.881	39	11.9	29
9.776	33	10.1	23
7.397	8	9.36	58
6.549	9	7.5	3
6.269	5	6.44	3
5.911	12	6.61	5
4.485	6	4.39	8
3.965	5	3.87	7
3.824	100	3.87	100
3.683	66	3.74	43
3.814	36	3.69	1
3.028	11	3.00	11
2.957	21	2.88	5
2.477	4	2.50	5
2.327	24	2.36	3
1.998	5	1.88	1
1.963	5	1.78	2
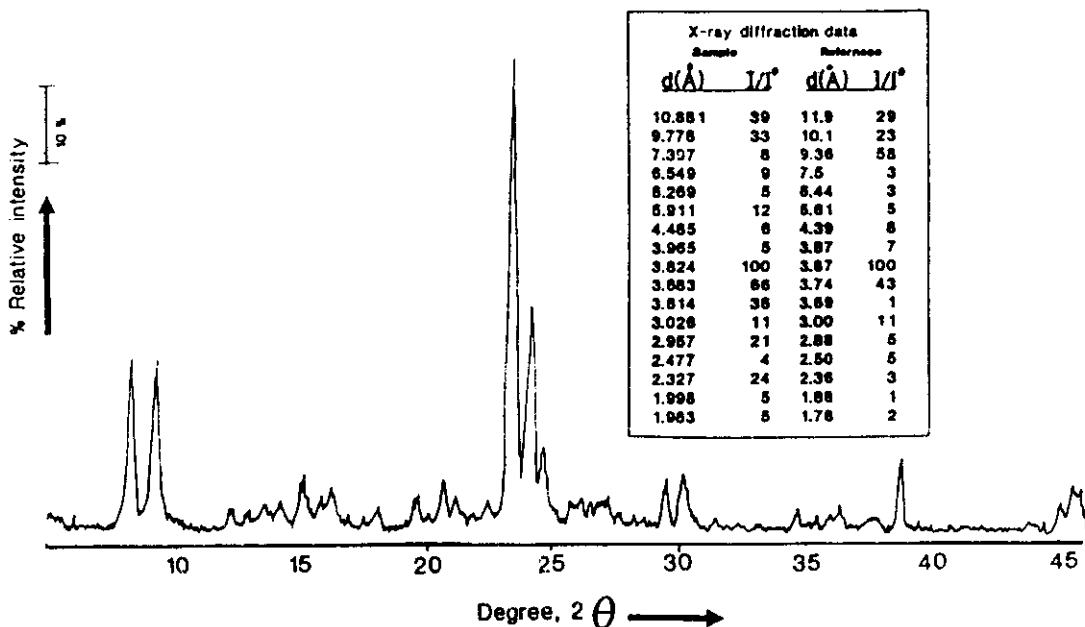
Fig. 6: X-ray powder diffraction pattern of zeolites, ZSM-5 (silicalite-1)

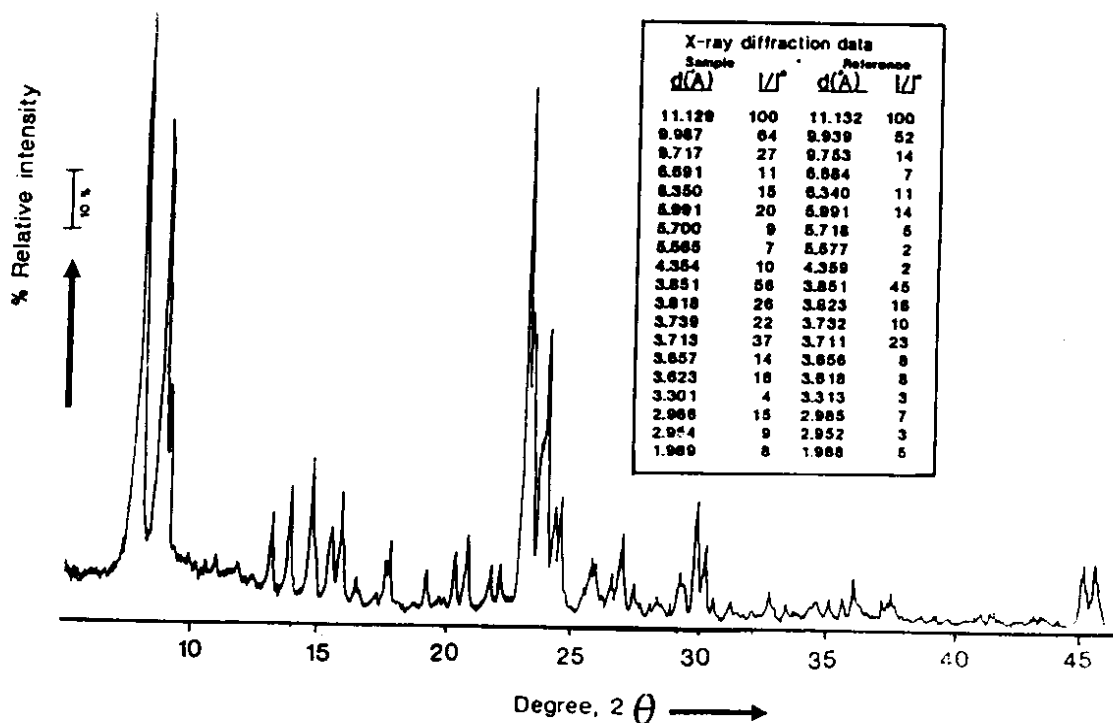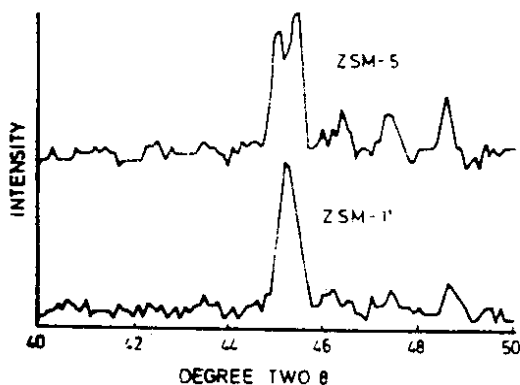| X-ray diffraction data			
Sample		**Reference**	
d(Å)	**I/I°**	**d(Å)**	**I/I°**
11.128	100	11.132	100
9.987	64	9.939	52
9.717	27	9.753	14
6.691	11	6.684	7
6.350	15	6.340	11
5.991	20	5.991	14
5.700	9	5.718	5
5.565	7	5.577	2
4.364	10	4.359	2
3.851	56	3.851	45
3.818	26	3.823	18
3.739	22	3.732	10
3.713	37	3.711	23
3.657	14	3.656	8
3.623	18	3.618	8
3.301	4	3.313	3
2.966	15	2.985	7
2.954	9	2.952	3
1.989	8	1.988	5

Fig. 7:   X-ray powder diffraction pattern of zeolite, ZSM-11 (silicalite-2)

Fig. 8:   Slow X-ray scan at 45 2θ to identify (a) ZSM-11 (silicalite-2) and (b) ZSM-5 (silicalite-1).

Adsorption of liquid hexane and cyclohexane

A property which is extensively used in characterising molecular sieve materials is the ability to sorb selected molecules. The most fundamental characteristic is the pore volume of the individual molecular sieve. Different techniques *i.e.* volumetric, gravimetric and temperature programmed desorption (constant coverage), and several probe molecules (oxygen, *n*-hexane and H$_2$O) have been used to measure the pore volume [18-20]. In the present work we have used constant coverage and thermogravimetric (TG-DTG) method for the determination of pore volume of high silica zeolites and their boron-zeotypes [13-14]. The TG-DTG thermograms of hexane and cyclohexane were analyzed. The results percent (%) amount of hexane and cyclohexane sorption and the number of molecules of hexane and cyclohexane per unit cell are presented in Table 1. The sorption capacity of a zeolite provides a measured of the void or pore volume. If the density of the adsorbate (liquid hexane) is assumed to be the same as that of the normal liquid phase *i.e.*, 0.6603 gml^{-1} the micropore volume (v$_{mic}$) in mlg^{-1} was calculated using Gurvitsch [20-21] rule. The quantity of material adsorbed at the point of

Table 2:   Micropore volue determined by constant coverage sorption of liquid hexane

Material	Thermal analysis			
	d$_z$ (g ml^{-1})	V$_{mic}$ (ml g^{-1})	V$_f$	V (Å^3)	V$_{Tmic}$ (Å^3/u.c)
SMS	1.772	0.167	0.296	5360	1587
SMS-B	1.892	0.165	0.312	5291	1652
SM11	1.837	0.174	0.319	5441	1736
SM11-B	1.905	0.167	0.318	5324	1693
ilicalite-1	1.834	0.162	0.298	5373	1402
ilicalite-2	1.841	0.164	0.303	5435	1646

d$_z$ = density of materials V = Unit cell volume from XRD V$_{mic}$ = micropore. volume V$_{Tmic}$ = Total pore volume Vf = void fraction V$_{Tmic}$ = V$_f$ V
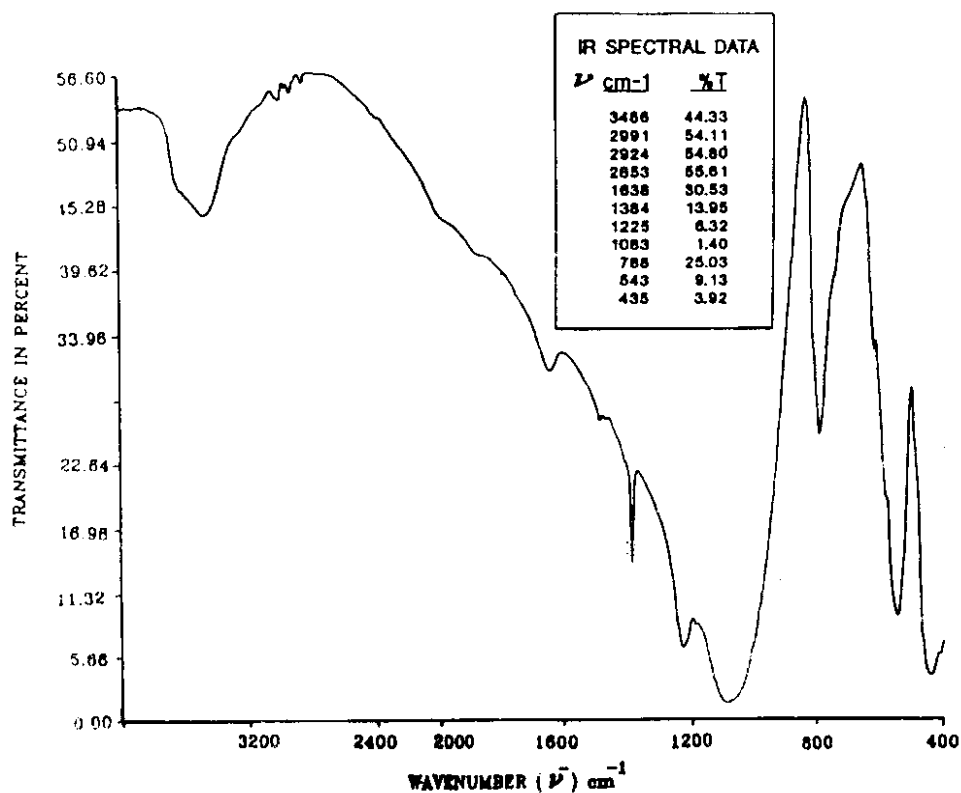
IR SPECTRAL DATA

ν cm-1	%T
3466	44.33
2991	54.11
2924	54.80
2853	55.61
1636	30.53
1384	13.95
1225	6.32
1083	1.40
788	25.03
543	9.13
435	3.92

Fig. 9:   Infared spectrum of zeolite ZSM-5 (as synthesised)

IR SPECTRAL DATA

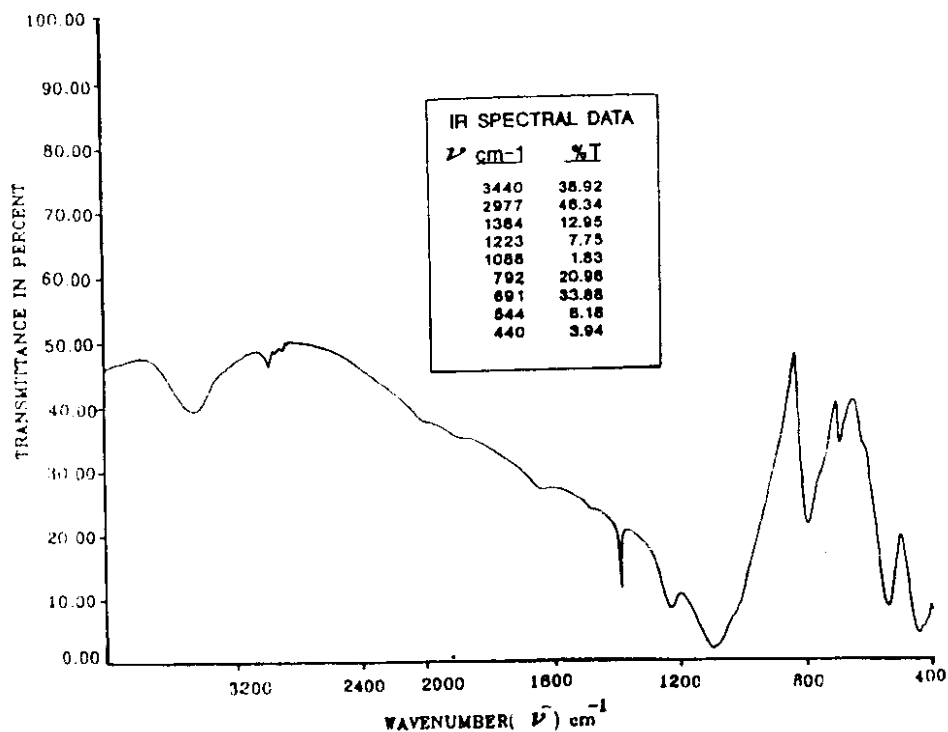| ν cm-1	%T
3440	38.92
2977	46.34
1384	12.95
1223	7.75
1088	1.83
792	20.96
691	33.88
544	8.18
440	3.94

Fig. 10:   Infrared spectrum of zeolite ZSM-11 (as synthesised

saturation, χ_s, is assumed to fill the pores of the solid as the normal liquid having a density d_a at that particular temperature. The total void volume of the micropores, V_{mic} is, therefore, given by:

$$v_{mic} = \chi_s / d_a \qquad (1)$$

where d_a, is the density of liquid sorbate (gml^{-1}), and χ_s is in g g^{-1}.

The densities and the micropore volume: V_{mic} from the sorption of liquid n-hexane by the constant coverage method for aluminosilicate high silica zeolites and boron-zeotypes are presented in Table 2. The crystal density of ZSM5, ZSM11 and their boron-zeotypes ZSM5-B, ZSM11-B and silicalites were found to be 1.777, 1.892, 1.837, 1.905, 1.8344 and 1.841 g cm^{-3} respectively. It may be noted the crystal density values were in close agreement with the theoretical value (1.785 g cm^{-3}) estimated from the framework density of ZSM5 17.9x10^{21} T (Si or Al cm^{-3}) [22]. As ZSM5, ZSM11), and their boron-zeotype (ZSM5-B, ZSM11-B) are hydrophobic and organophilic, sorption of organic molecules occurs through the filling of micropores by physical sorption at low relative pressure. The resuls of Table-1 indicate that the amount of n-hexane and cyclohexane sorption was higher in ZSM11 than ZSM5. The same is true for ZSM11-B and ZSM5-B. These results were consistent with the work of Rees and coworkers [23]. ZSM5 and ZSM11 both belong to the pentasil family, ZSM11 contains two sets of straight channels, orthogonal and intersecting [5] while ZSM5 contains one set of similar channels that are intersected orthogonally by another set of sinusoidal channels, [5] as shown in Figures (4-5). In ZSM5 the cavities are all equivalent, whereas in ZSM11, there are two types of cavities, one which is very nearly the same as that which occurs in ZSM5, while the other has about 30% greater volume, [24-25] which accounted for the greater sorption capacity of ZSM11. The n-hexane was sorbed readily in the zeolites having 10-ring structure and also in the 12-ring zeolites (BETA and BETA-B) whereas cyclohexane sorption was found to be very high in 12-ring zeolite as compared to 10-ring zeolite (ZSM5 and ZSM11) [26]. The values of pore volume were found to be close agreement with those reported earlier [15]. Barrer and coworkers [27] observed that n-paraffins were excluded from the main sorption channels of a sodium mordenite. However, others

have shown that the main channels are available to neopentane. Smaller gas molecules voids in addition to the main channels; must include the small, niche-type cavities which lie on the side of the main c-axis channels. Replacement of sodium cations by hydrogen opens the channels so that more space is available, to some of the larger hydrocarbon molecules. Consequently, the total pore volume in the mordenite is about 0.21 ml g^{-1} with 0.11 ml g^{-1} in the main channels only. It has been observed that at a relative pressure $\rho/\rho°$ equal to 0.5 the sorption of paraffin hydrocarbon by zeolites follows the Gurvitsch rule very well [28-29]. The sorption of hydrocarbons allows us to characterize the dimension and tortuosity of the zeolite channels. From the knowledge of the amounts sorbed, using molecular dimensions and assuming an end-to-end configuration of the sorbed molecules one can evaluate the channel length occupied per unit cell by the adsorbate. To carry out these measurements we have chosen a linear paraffin molecule such as n-hexane (C_6). The n-pentane molecule has been chosen due to the well known fact that isoparaffins [30] are adsorbed preferentially in the linear channels because their adsorption in the sinusoidal channel is somewhat hindered. The kinetic diameter of n-hexane is 43 nm and less than the free diameter of 10-ring zeolites. From the n-hexane uptake we may calculate the total length occupied by the sorbed n-hexane molecule in high silica zeolites and their boron-zeotypes, and our results are given in the Table 3. The total lengths occupied by the n-hexane molecule in ZSM5 and ZSM5-B were found to be 7.89 and 7.69 nm/unit cell respectively. This indicates that n-hexane molecules were sorbed in an end-to-end arrangement with seemingly only one molecule per intersection. Similarly the total channel length per unit cell occupied by n-hexane molecules in zeolites ZSM11 and ZSM11-B were found to be 8.2 and 7.83 nm/unit cell respectively, again indicating only one molecule per intersection. The ZSM5 and silicalite-1 framework contains two types of intersecting channels: one channel system which is sinusoidal and has near circular (0.54-0.56 nm) opening, the other channel system is straight and has near elliptical opening (0.52-0.58 nm), Figure (3-5). It has been observed that total channel length of the pore system per unit cell (sinusoidal, near-circular channel plus linear, elliptical channels) is 8.8 nm, if two molecules are accomodated per intersection, whilst that of the linear elliptical channels alone is 6.65 nm/unit cell,

Table 3: Effective channel length occupied by *n*-hexane molecule (nm/u.c) in high silica zeolite and their boron-zeotypes.

Materials	Temp (K)	Kinetic diameter (nm)	Chain lenght (nm/uc)	Molecules per unit cell	Adsorbate chain length hexane (nm)	Effective length (nm/u.c)
ZSM5	298	0.43	8.8	7.64	1.034	899
ZSM5-B	298	0.43	8.8	7.44	1.034	693
ZSM11	298	0.43	8.0	7.94	1.034	209
ZSM11-B	298	0.43	8.0	7.57	1.034	827
Silicalite-1	298	0.43	8.8	8.01	1.034	282
Silicalite-2	298	0.43	8.0	7.93	1.034	827

Values of kinetic diameter (nm) are taken from Handbook of Chemistry and Physics, CRC Press. Cledveland, Ohio, U.S.A. (1968).

with only one molecule per intersection [2,5,19,23]. The results of the Table-3 show that typical values of total length of adsorbates in pores measures for most of our samples vary from 7.69 to 8.2 nm indicating a good agreement with the total length of the pore system per unit cell *i.e.* 8.8 nm for zeolites (ZSM5, ZSM11) and zeotypes (ZSM5-B, ZSM11-B) and silicalites with different Si/M ratios. Vedrine *et al.* [31] has observed that in the Penatasil framework, the adsorption capacities of *n*-hexane and *p*-xylene are close to 8 molecules per unit cell, and 5 molecules per unit for 3-methyl-pentane, indicating that the *n*-hexane and the *p*-xylene gain access to both channel systems, while the branched paraffin, due to its size, has a restricted adsorption in the sinusoidal channel. Cyclohexane molecule has a kinetic diameter only slightly larger then the channel, but its rigid configuration causes the diffusion to be very slow at room temperature.

Table 4: Unit cell parameters and unit cell volumes of high silica zeolites and boron-zeotypes

Materials	a(Å)	b(Å)	c(Å)	V(Å 3)
ZSM5	20.08 ± 0.01	19.91 ±0.01	13.41 ± 0.01	5361
ZSM5-B	20.0 ± 2 0.01	19.80± 0.01	13.35 ±0.01	5292
ZSM11	20.11 ± 0.01	20.11 ±0.01	13.44 ±0.01	5441
ZSM11-B	19.96 ±0.01	19.96 ±0.01	13.35 ± 0.01	5324
Silicalite-1	20.05 ±0.01	19.79 ± 0.01	13.37 ± 0.01	5305
Silicalite-2	20.11 ±0.01	20.11 ±0.01	13.44±0.01	5435

Unit cell parameters and unit cell volume were calculated from x-ray diffraction d-spacing values using least squares refinement [32-33] on 386/IBM Personal Computer with the help of Ital Structure data analysis software. Unit cell parameters and unit cell volumes of silicalite, high silica zeolites and their boron-zeotypes are summarised in Table-4. Reduction of unit cell dimensions because of the smaller size of B^{3+} (0.011 nm) relative to Al^{3+} (0.039 nm) is one of the strongest arguments for the belief that the B is located substitutionaly in the lattice rather than in the channels. The cell dimension of B-substituted sample are significantly smaller than those of the Al-substituted samples. This is in agreement with results of other investigators [34]. Results of sorption capacity of the boron-zeoptypes are compared with those of ZSM5-Al and ZSM11-Al. Although ZSM5-Al and ZSM5-B sorb similar quantities of smaller molecules like *n*-hexane, ZSM11-Al adsorbed signifcantly greater quantities of the larger molecules than the Al forms. This shows that differences in the void volume due to boron incorporation in the lattice are very small; this agrees with the slight changes not'd in the unit cell volumes. In contrast, differences between ZSM-5 and ZSM-11 are more significant; this is perhaps due to larger channel intersections in ZSM-11.

Conclusion

It is emphasized, that the sorption of normal paraffin efficiently probes the entire void space, while large molecules are excluded from the zig-zag channels. Pentasil zeolites possesses distinct sorption properties with a channel size intermediate between small (8-ring) and large pore (12-ring) zeolites. Hydrocarbon sorption by 8-ring zeolites is essentially limited to normal paraffins while 12-ring zeolites can sorb molecules as large as tributlamine (91 nm). While ZSM-5 sorbs molecules are large as *o*- and *m*-xylene and 1,2,4-trimethylbenzene, all having minimum diameter of ~69 nm.

The molecular sieving effect of silicalite depends mainly on the relative size of the channel and the diameter and the configuration of the adsorbate. *N*-paraffins molecules such as *n*-hexane rapidly sorbed into silicalite and are packed in the channels with a higher density due to their small diameter and elastic configuration

Experimental

All the chemicals used were high purity grade. The zeolites and zeotypes were synthesised according to published methods [3-7]. The characterization of these materials were carried out by XRD, SEM, FTir, TG/DTG and DSC

techniques and are fully described elsewhere [12]. Sorption of liquid *n*-hexane and cyclohexane in high silica aluminosilicate zeolite and boron-zeotypes was carried out according to published method [13-14]. Liquid cyclohexane and hexane were placed in the bottom of a desiccator and the zeolites were placed above the liquid surface immediately after outgassing at 723° K. The zeolites were kept in the desiccator for at least 7 days, before the thermogravimetric weight loss measurement. Organic molecule and water contents were observed by thermogravimetry using a Mettler M3-TG50 thermobalance. Density was measured by mercury porosimeter.

Acknowledgements

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